

# CALCIUM CARBONATE DISSOLUTION IN THE PACIFIC OCEAN

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## ABSTRACT

As a part of the JGOFS synthesis and modeling project, researchers have been working to synthesize the WOCE/JGOFS/DOE/NOAA global CO<sub>2</sub> survey data to better understand carbon cycling processes in the oceans. Working with international investigators we have compiled a Pacific Ocean data set with over 35,000 unique sample locations analyzed for at least two carbon species, oxygen, nutrient, CFC tracers, and hydrographic parameters. These data are being used to determine the rates of in-situ CaCO<sub>3</sub> dissolution in the water column of the Pacific Ocean. Calcium carbonate dissolution rates (ranging from about 0.05 – 1.1 μmol kg<sup>-1</sup>yr<sup>-1</sup>) are observed in the intermediate and deepwater depths beginning near the aragonite saturation horizon. Within the North Pacific Intermediate Water (depth range: 400 – 800 m), CaCO<sub>3</sub> dissolution rates are more than 7 times faster than observed in mid- and deepwater depths (average = 0.051 μmol kg<sup>-1</sup>yr<sup>-1</sup>) of the North Pacific.

## 1. INTRODUCTION

In recent years, concern about the long-term fate of anthropogenic CO<sub>2</sub> in the atmosphere and oceans has prompted oceanographers to re-examine the fundamental processes controlling the distributions of dissolved inorganic carbon (DIC) and total alkalinity (TA) in the oceans. The primary motivation for this research is that processes that increase the alkalinity into the upper ocean help to facilitate the uptake of anthropogenic CO<sub>2</sub> from the atmosphere. Conversely, processes that reduce the alkalinity serve to impede the uptake. Marine carbonates, including calcitic (e.g., coccoliths and forams) and aragonitic (e.g., pteropods) marine plankton neutralize anthropogenic CO<sub>2</sub> via the dissolution reaction:



The increase in alkalinity (A) from this reaction serves to enhance the ocean's capacity for absorbing more CO<sub>2</sub> from the atmosphere. The primary contributors to this reaction will be the carbonate shells of marine plankton, which are produced in the euphotic zone, fall through the water column, and are deposited in shallow and deep-sea sediments. As the oceans become enriched in anthropogenic CO<sub>2</sub>, the locations and extent of dissolution will increase as a function of changes in the CaCO<sub>3</sub> saturation state. Until recently, it has been commonly thought that dissolution of pelagic calcium carbonate particles only occurs at great depths below the “carbonate lysocline” (Sverdrup et al., 1941). However, a recent analysis of sediment trap data for the global oceans by Milliman et al (1999) has suggested that perhaps as much 60 – 80% of the calcium carbonate that is exported out of the surface ocean dissolves in the upper 500–1000 m, well above the carbonate lysocline. In this paper we examine the WOCE/JGOFS/DOE/NOAA global CO<sub>2</sub> survey data from the Pacific Ocean and provide new estimates of calcium carbonate dissolution rates in the water column based upon changes in TA.

## 2. THE WOCE/JGOFS/OACES DATA

Between 1991 and 1996, carbon measurements were made on twenty-four cruises in the Pacific Ocean. This research was a collaborative effort between 15 laboratories and 4 countries. At least two carbon parameters were measured on almost all cruises, but the choice of which carbon pairs were measured varied between cruises. The quality of the carbon data was evaluated by Lamb et al. [2001]. A set of adjustments for certain cruises were recommended based on many lines of evidence including comparison of calibration techniques, results from certified reference material analyses, precision of at-sea replicate analyses, agreement between shipboard analyses and replicate shore-based analyses, comparison of deep water values at locations where two or more cruises overlapped or crossed, consistency with other hydrographic parameters, and internal consistency with multiple carbon parameter measurements. They estimated that the overall accuracy of the dissolved inorganic carbon (DIC) data was ~ 3 μmol kg<sup>-1</sup>. Total alkalinity, the second most common carbon parameter

analyzed, had an overall accuracy of  $\sim 5 \mu\text{mol kg}^{-1}$ . The TA was calculated for all cruises where TA was not measured using DIC and  $\text{pCO}_2$  or DIC and pH measurements together with the carbonate dissociation constants of Merbach [1973] as refit by Dickson and Millero [1987] and ancillary constants listed in the program of Lewis and Wallace [1998]. The final data set contained about 35,000 sample locations with DIC and TA values.

The corresponding chlorofluorocarbon (CFC) data were compiled and evaluated by the US WOCE CFC consortium. The Pacific synthesis of the chlorofluorocarbon data, lead by J. Bullister, examined the overall quality of the data and ensured that all of the values were reported on the same concentration scale. Although no adjustments were made to the final reported CFC values, the data were carefully flagged based on examination of the entire data set.

### 3. ANALYSIS METHOD

The observed distribution of TA in the water column has two components: (1) the preformed fraction ( $\text{TA}^\circ$ ) of TA, the values of TA when a parcel of water was last in contact with the atmosphere; and 2) the TA added to the water column due to  $\text{CaCO}_3$  dissolution. Thus, for a given isopycnal surface, subtracting  $\text{TA}^\circ$  from the measured TA (corrected for release of protons from the oxidation of organic matter) gives a measure of the TA due to  $\text{CaCO}_3$  dissolution. In this study we employed the method Sabine et al. (1999) to estimate the preformed alkalinity from near surface (0 – 60 m) data in the Pacific according to the following equation:

$$\text{TA}^\circ = 136.7 + (61.64 \cdot S) + (0.1004 \cdot \text{PO}) - (0.574 \cdot \theta) \quad (2)$$

where S is the salinity,  $\text{PO} = \text{O}_2 - \text{R}_{\text{O}_2/\text{P}} \cdot \text{HPO}_4^{2-}$  (after Broecker, 1974), and  $\theta$  is the potential temperature. An  $\text{O}_2/\text{P}$  ratio of 170 is used in this work (Anderson and Sarmiento, 1994). The amount of  $\text{CaCO}_3$  dissolved is then calculated with the equation:

$$\text{CaCO}_{3\text{dis}} = 0.5 (\text{NTA} - \text{NTA}^\circ) + 0.63(0.0941 \cdot \text{AOU}) \quad (3)$$

where  $\text{NTA} = (\text{TA} \cdot 35)/S$  and AOU is the apparent oxygen utilization. This approach has been used successfully by previous investigators with good success (Chen, 1990; Sabine et al., 1995).

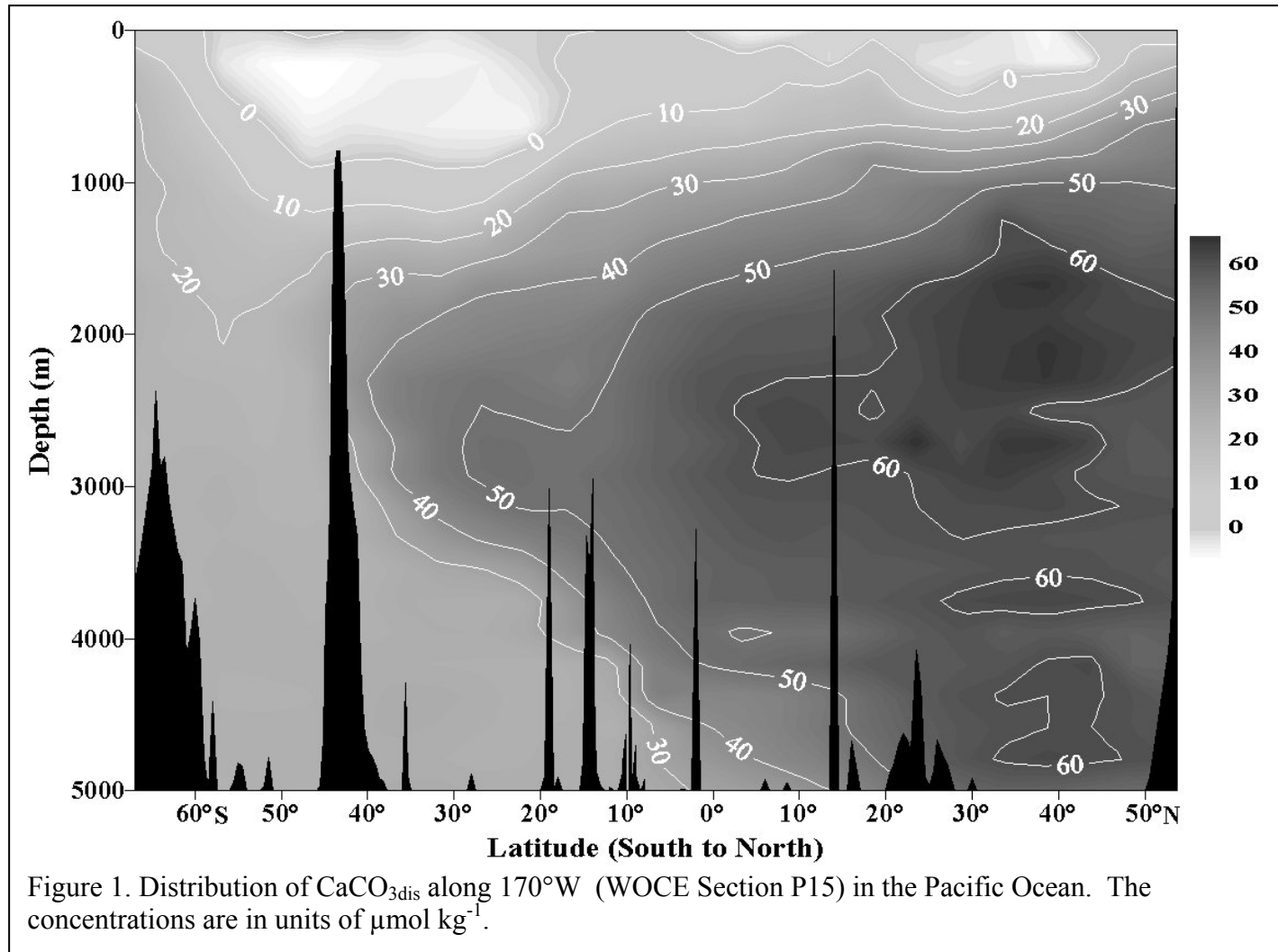
### 4. RESULTS AND DISCUSSION

The WOCE/JGOFS/DOE/NOAA global  $\text{CO}_2$  survey in the Pacific were used for estimating  $\text{CaCO}_3$  dissolution in the water column. Figure 1 shows a meridional section of  $\text{CaCO}_{3\text{dis}}$  along  $170^\circ\text{W}$ . Positive concentrations of  $\text{CaCO}_{3\text{dis}}$  are observed in the shallow waters of the North and South Pacific close to or slightly above the aragonite saturation horizon. Immediately below this horizon, concentrations of  $\text{CaCO}_{3\text{dis}}$  increase rapidly from 10 - 40  $\mu\text{mol kg}^{-1}$ . This large increase is primarily located in the Intermediate Waters of the North and South Pacific. For example, in the North Pacific north of  $20^\circ\text{N}$  the largest increase occurs between about 400 - 1100 m where the  $\text{CaCO}_{3\text{dis}}$  increase is from  $<10 \mu\text{mol kg}^{-1}$  in the central North Pacific to values  $> 40 \mu\text{mol kg}^{-1}$  north of  $40^\circ\text{N}$ . In the South Pacific, where the aragonite and calcite saturation horizons are much deeper, the largest increases are from about 800 m to 2000 m between  $10^\circ\text{S}$  and  $45^\circ\text{S}$ . Further south, the increase in  $\text{CaCO}_{3\text{dis}}$  begins at much shallower depths, consistent with the shoaling of the aragonite saturation horizon. These results suggest that the extent of  $\text{CaCO}_3$  dissolution is related, to some extent, to the degree of aragonite saturation.

Combining the above results with the apparent CFC-11 age data from the WOCE global survey data on isopycnal surface allows us to calculate the  $\text{CaCO}_3$  dissolution rates by plotting  $\text{CaCO}_{3\text{dis}}$  versus apparent CFC-11 ages.  $\text{CaCO}_3$  dissolution rates calculated in this manner range from 0 in shallow waters to a maximum of  $1.1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  in the Subantarctic Intermediate Water of the South Pacific. The shallow water dissolution rates reach a maximum in the Intermediate Waters and then decrease rapidly thereafter. Since the CFC-age method is limited to water mass ages less than about 40-45 years, we shifted to natural  $^{14}\text{C}$  ages from samples collected on the same cruises to estimate  $\text{CaCO}_3$  dissolution rates in deeper waters. The  $^{14}\text{C}$  decay rate of 1% every 83 years makes this isotope a perfect age tracer for dissolution processes in the deep sea. For waters  $> 1000$  m the mean  $\text{CaCO}_3$  dissolution rate in the Pacific Deep Water was determined to be  $0.051 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ . Higher dissolution fluxes were observed in the South Pacific relative to the North Pacific.

Table 1 shows the comparison of the new results from the WOCE survey with the results from earlier expeditions. In shallow waters (100 – 1100 m), the mean  $\text{CaCO}_3$  dissolution rate from the WOCE results,  $0.36 \mu\text{moles kg}^{-1} \text{yr}^{-1}$ , is within the range of estimates from the sediment trap data ( $0.005 - 1.83 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ). For water  $> 1000$  m the mean  $\text{CaCO}_3$  dissolution rate ( $0.051 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ) is near the middle of the range of estimates from the previous estimates ( $0.0 - 0.11 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ). The average  $\text{CaCO}_3$  dissolution rate in the shallow waters of the North Pacific is 7.4 times faster than the

deep-water dissolution rates. These results are slightly lower than the  $\text{CaCO}_3$  dissolution rates calculated from the sediment trap data reported in Milliman (1999).



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## 5. CONCLUSIONS

The new results from the WOCE/JGOFS/DOE/NOAA global  $\text{CO}_2$  survey in the Pacific Ocean indicates that water column dissolution of  $\text{CaCO}_3$  in shallow waters <1100 m accounts for as much as 50% of the total dissolution in the water column, consistent with the reanalysis of the sediment trap data by Milliman et al. (1999). These results imply that the re-supply of alkalinity to the surface waters via shallow water remineralization processes may occur at faster rates than previously thought. The long-term impacts of this dissolution process on the oceans ability to neutralize anthropogenic  $\text{CO}_2$  need to be given consideration in future models.

Table 1. *In-situ* Calcium Carbonate Dissolution Rates in the Pacific Ocean.

Study Reference	Depth Range (km)	CaCO <sub>3</sub> Dissolution Rate (μmol kg <sup>-1</sup> yr <sup>-1</sup> )
<u>Deep Water Column</u>		
Li et al. (1969)	> 1	0.09
Tsunogai (1972)	> 1	0.048
Tsunogai et al. (1973)	< 4	0.04 and 0.11
Edmond (1974)	< 5	0.048
Fiadeiro (1980)	> 1	0.06
Tsunogai and Watanabe (1981)	> 1	0.057
Feely et al. (1986) (A <sub>T</sub> and Ca data)	> 1	0.06
Chen (1983; 1990)	> 2	0.072
Chen (1983) (A <sub>T</sub> data)	> 2	0.053
Chen (1983) (Ca data)	> 2	0.06
Sabine et al. (A <sub>T</sub> data: this study)	> 1.0	0.051
<u>Deep Sediment Trap Studies</u>		
Tsunogai and Noriki (1991)	0.5-1	0.02
	1-2	0
	2-3	0.006
	3-4	0.003
	4-5	0
<u>Equatorial Pacific</u> (Honjo et al, 1995)		
5°N	2.2-3.9	0.014
EQ	2.3-3.6	0.008
12°S	1.3-3.6	0.005
<u>Shallow Water Dissolution</u>		
Honjo et al. (1995) Traps (spring)	0.1-1	1.83
Betzer et al. (1984)	0.1-1	0.12
Rodier and LeBorgne (1997) Floating traps	0.1-0.32	0.68
Milliman et al. (1999)	0.35-0.5	1.56
Feely et al. (this study, DIC, A <sub>T</sub> , O <sub>2</sub> data)	0.2-1.1	0.36

## 6. REFERENCES

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